

# Triarylamine-enchained semifluorinated perfluorocycloalkenyl (PFCA) aryl ether polymers

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**Abstract** A variety of perfluorocycloalkenyl (PFCA) aryl ether monomers and polymers with enchained triarylamine units were successfully synthesized, characterized and reported here. These polymers are highly thermally stable and show variable thermal properties. Successful conversion of the newly synthesized TAA enchained perfluorocyclopentenyl (PFCP) aryl ether polymers via formylation and EAS demonstrates the synthetic versatility of TAA moiety and provides an excellent option for application specific post polymerization reactions. The cross-linking behavior of PFCP aryl ether polymers was studied under different reaction conditions. The combination of processability, thermal stabilities, and tailorability makes these polymers suitable for a wide variety of applications including electro-optics, proton exchange membranes and super-hydrophobic applications.

**Keywords** Semi-fluorinated polymers · Step-growth polycondensation · Addition–elimination reaction · Perfluorocycloalkenes

## Introduction

The serendipitous discovery of poly(tetrafluoroethylene) by Roy Plunkett caught the global attention and led to tremendous improvement in fluoropolymer field [1, 2]. Due to their high thermal and chemical stabilities, fluoropolymers are regarded for adverse applications. Fluoropolymers also exhibit low refractive index and fraction coefficient, low optical loss at telecom wavelength, good hydrophobicity and oleophobicity, low intermolecular and intramolecular interactions, which result in low surface energy and low relative permittivity [3, 4]. Crediting to these properties, fluoropolymers have shown their use in a variety of applications including paints and coatings, optical fibers, antifouling coatings, materials for photoresist and micro-lithography, conducting polymers, aerospace, and wire and cable industry materials [5–19].

Due to their high crystalline nature, high melting point and the low solubility problem, the processability of these fluoropolymers is difficult. The modification of these fluoropolymers to high performance materials without melt and solution processing limitations demands high cost. There is always a constant demand for fluoropolymers with cheaper feed stocks, variable thermal properties and excellent properties. Although, majority volume of fluoropolymers is derived via chain growth polymerization of fluorinated olefin monomers, step growth polymerization methodology also has been used. Perfluorocyclobutyl (PFCB) aryl ether polymers and fluorinated arylene vinylene ether (FAVE) polymers are two such classes, synthesized via step growth polymerization of aromatic trifluorovinyl ether (TFVE) monomers (Scheme 1). [20–24] The aromatic backbones in these semifluorinated polymers not only address the performance issue, but also

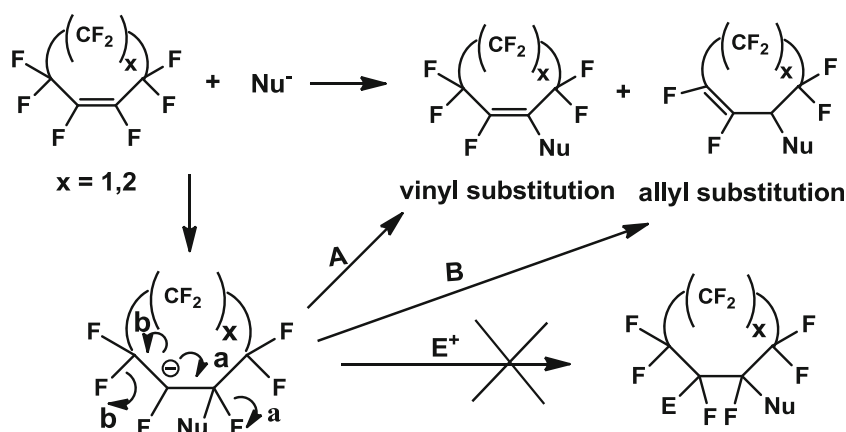
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**Scheme 3** Nucleophilic attack on PFCA rings leads to vinyl and allyl products [28]



fluorocycloalkenyl (PFCA) aryl ether polymers with triarylamine moieties, and cross-linking behavior of PFCA aryl ether polymers. TAA moieties provide an excellent reaction site for post polymerization modification to make these fluoropolymers application specific [26, 29].

## Results and discussion

### Step-growth polymers: methodology

PFCP aryl ether polymers and PFCH aryl ether polymers are synthesized via step-growth polymerization of commercially available bisphenols with octafluorocyclopentene (OFCP) and decafluorocyclohexene (DFCH), respectively (Scheme 2) [27, 28]. In optimized reaction condition, the bisphenols are mixed with perfluorocycloalkene (PFCA) monomers in a stoichiometric ratio of 1:1 and heated at 80 °C in the presence of a base, triethylamine. This method produces PFCA aryl ether polymers with enchain perfluoro-olefin moieties intact, in good yield.

Nucleophilic attack on a perfluoro-olefin is a well studied and documented organofluorine transformation and continues to attract attention periodically [30]. Here, attack on PFCA ring by phenoxide ion, resulted in situ due to action of base on bisphenol, generates a carbanion on perfluorocycloalkene ring which, theoretically, can eliminate fluoride ion resulting in allyl and vinyl substituted products (Scheme 3). However, as the literature demonstrates, the ratio of vinyl to allyl substituted products varies and depends on the PFCA ring size, nucleophilicity of attacking anion, and reaction conditions. [28, 31, 32].

### Synthesis and characterization

PFCP aryl ether polymers derived from the OFCP gave exclusively vinyl fluoro-olefin enchainments, no trace of allyl product was noticed [27]. However, the PFCH aryl

ether polymers prepared from DFCH gave both, vinyl fluoro-olefins as major and allyl fluoro-olefins as minor enchainments via a double addition–elimination mechanism [28].

Gel permeation chromatography (GPC) showed number-average molecular weights ( $M_n$ ) from 9,100 to 15,400 for PFCP aryl ether polymers derived from different bisphenols [27]. In case of PFCH aryl ether polymers,  $M_n$  ranged from 9,400 to 15,600 [28]. Thermogravimetric analysis (TGA) showed excellent thermal stability of these polymers. The degradation temperature at 5 % weight loss ( $T_d$  5 %) varied from 432 to 483 °C and 383 to 444 °C for PFCP aryl ether polymers and PFCH aryl ether polymers, respectively. Thermal analysis via differential scanning calorimetry (DSC) showed variable glass transition temperature ( $T_g$ ) ranging from 432 to 483 °C and 90 to 132 °C for PFCP aryl ether polymers and PFCH aryl ether polymers, respectively. Interestingly, both PFCA aryl ether polymers synthesized from Bisphenol-AF also showed melting peaks in their respective DSC thermogram. This anomalous crystalline nature was attributed to a higher fluorine content, as found with  $-\text{C}(\text{CF}_3)_2$  moiety of the bisphenol-AF group [33].

In this manuscript, PFCP aryl ether monomer and polymers with enchain triarylamine (TAA) units were synthesized and studied (Scheme 4, 5). The latent reactivity of TAA unit provides the post polymerization modification opportunities to achieve application specific properties Scheme 6.

Bis(4-methoxyphenyl)phenylamine (A) and its deprotected analogous (B) were prepared by following the standard literature procedure via Ullman coupling (i) and  $\text{BBr}_3$  methoxy deprotection (ii), respectively [26, 34, 35]. The bis(perfluorocyclopentenyl)oxy)triarylamine monomer (M) was synthesized by treating B with OFCP in a stoichiometric ratio of 1:3 in the presence of a base, triethylamine at room temperature (Scheme 4).  $^{19}\text{F}$  NMR shows only three distinct resonances (8:4:2) corresponding to three different fluorine atoms (Fig. 1). As expected, PFCA

Chemical reaction scheme showing the synthesis of Monomer (M):

Starting materials: Aniline (NH<sub>2</sub>) and 2 equivalents of 4-iodoanisole (1) react under conditions (i) to form intermediate (A), N,N'-bis(4-methoxyphenyl)-N,N'-diphenylbenzidine.

Intermediate (A) is converted under conditions (ii) to intermediate (B), N,N'-bis(4-hydroxyphenyl)-N,N'-diphenylbenzidine.

Intermediate (B) is converted to Monomer (M), N,N'-bis(4-(2,3,4,5-tetrafluorophenoxy)phenyl)-N,N'-diphenylbenzidine.

Monomer (M) + HO-Ar-R-Ar-OH  $\xrightarrow[80\text{ }^{\circ}\text{C}]{\text{NEt}_3, \text{DMF}}$  Polymer

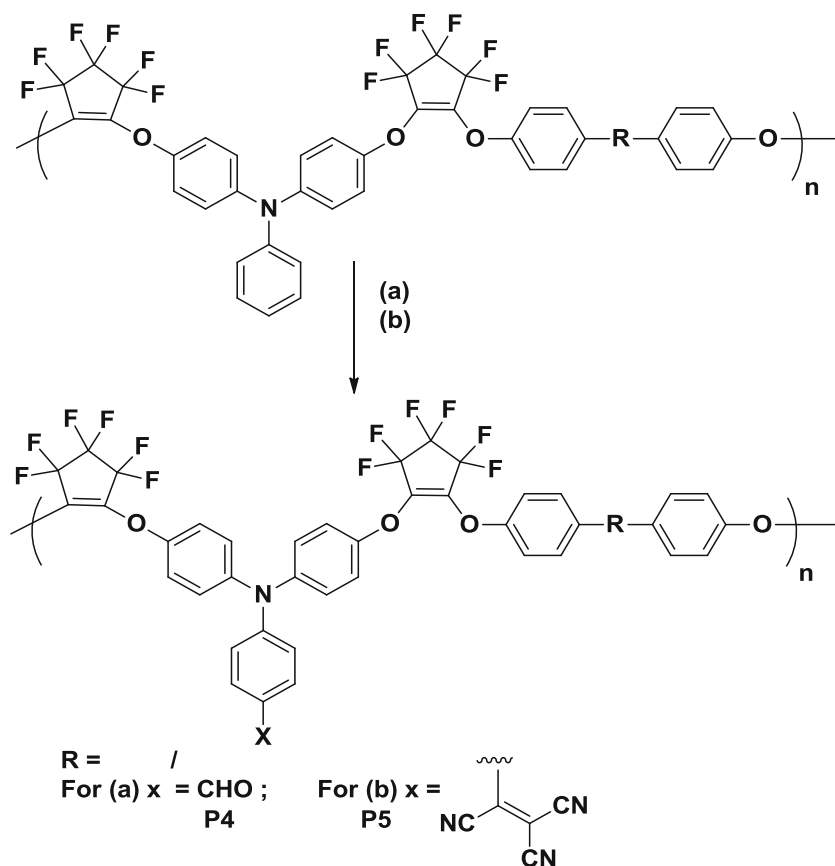
R =  $\text{—}$  (P1),  $\text{—C(CH}_3\text{)}_2\text{—}$  (P2),  $\text{—C(CF}_3\text{)}_2\text{—}$  (P3)

amount of allyl substitution along the polymer chain (Figs. 2, 3s, 5s). Thermal stabilities for these polymers chain studied via TGA analysis. The decomposition temperature ( $T_d$  at 5 % weight loss, in nitrogen atmosphere) ranges from 370 to 456 °C (Fig. 3). The impressive degradation temperatures ( $T_d$  5 %) up to 450 °C are typical for PFCP aryl ether polymer systems [27]. Thermal analysis via differential scanning calorimetry (DSC) shows the polymers show variable glass transition temperature ( $T_g$ ) depending on the bisphenol used. The  $T_g$  for these polymers ranges from 87 to 106 °C (Fig. 4). There was no sign of melting peak, as expected.

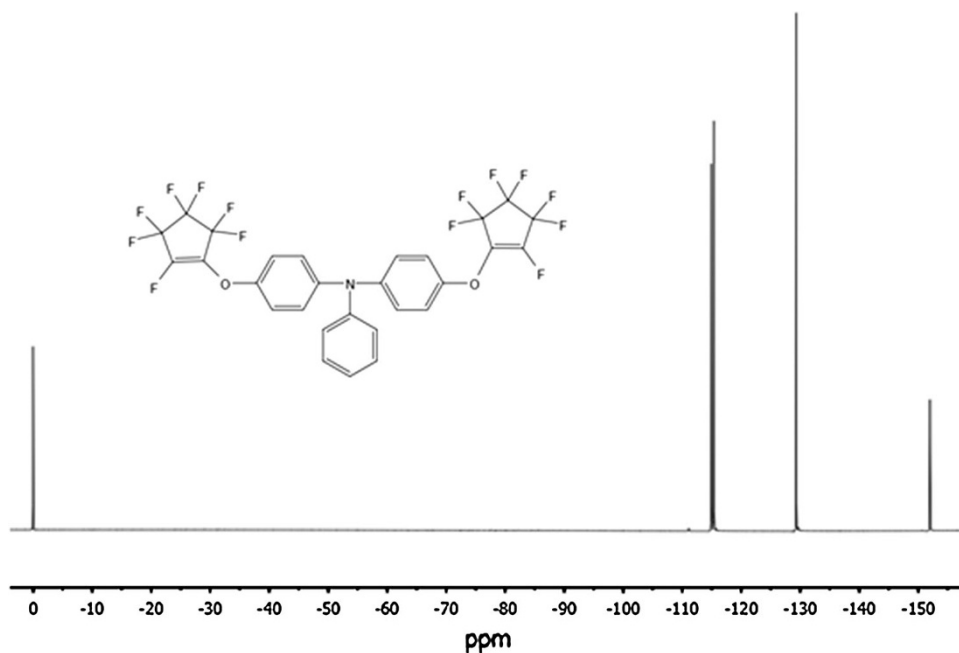
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**Scheme 6** Post polymerization modification (i.e. chromophorization) of PFCP-TAA ether polymer



**Fig. 1**  $^{19}\text{F}$  NMR for monomer **M**



on an inert polymer backbone] is an excellent tool to make a polymer system application specific. Here, we have post-functionalized PFCP aryl ether polymer with enchain TAA moieties via formylation and electrophilic aromatic

substitution (EAS) (Scheme 6). Successful conversion of the TAA enchain PFCP polymers via formylation and EAS demonstrated the synthetic versatility of TAA moiety. All these reported reactions resulted in high yields. The

**Table 1** PFCP aryl ether polymers with enchainned triarylamine unites

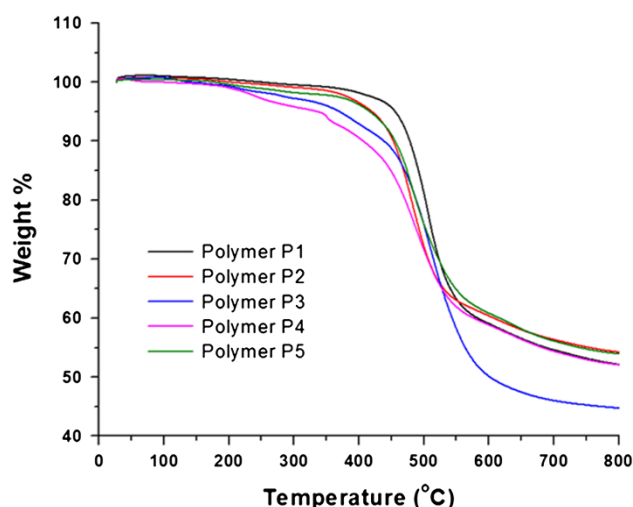
Entry	$M_n$	$M_w$	PDI	$T_d$ 5 % (°C)	$T_g$ (°C)
Polymer P1	23,600	36,800	1.4	456	99
Polymer P2	11,100	18,500	1.6	420	87
Polymer P3	22,100	36,000	1.6	370	106
Polymer P4	14,100	26,500	1.8	337	101
Polymer P5	17,200	32,100	1.8	416	100

incorporated aldehyde (**P4**) can be further modified into a range of application-specific molecules, including extension into an EO chromophore, hole-transport and photovoltaic materials [29, 34, 36, 37]. EAS reaction on these PFCP aryl ether polymers demonstrates the accessibility of these TAA moieties for further post polymerization modifications, which extends the overall versatility of this polymeric system.

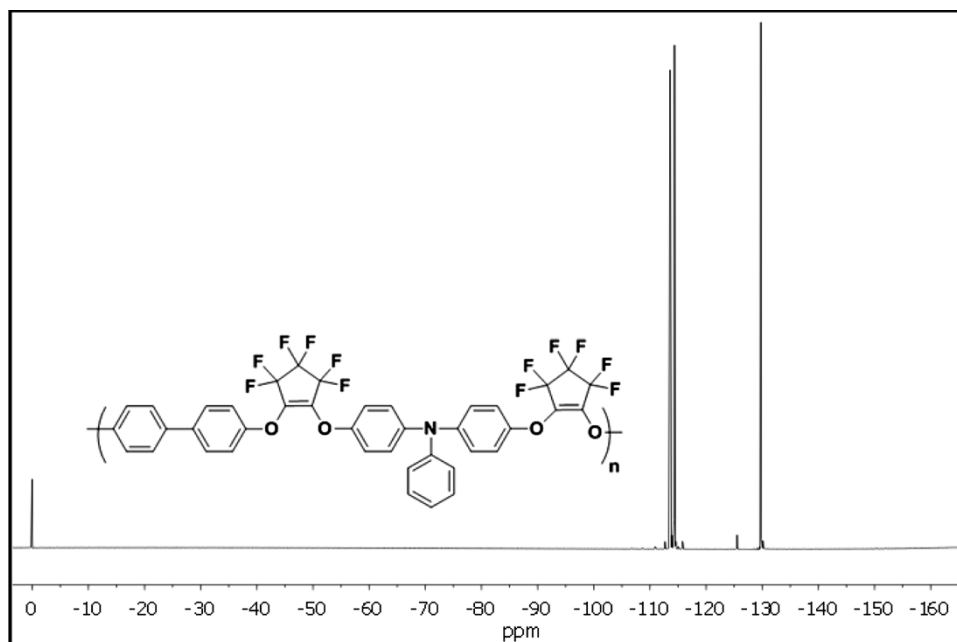
### Network polymers: cross-linking behavior of PFCA polymers

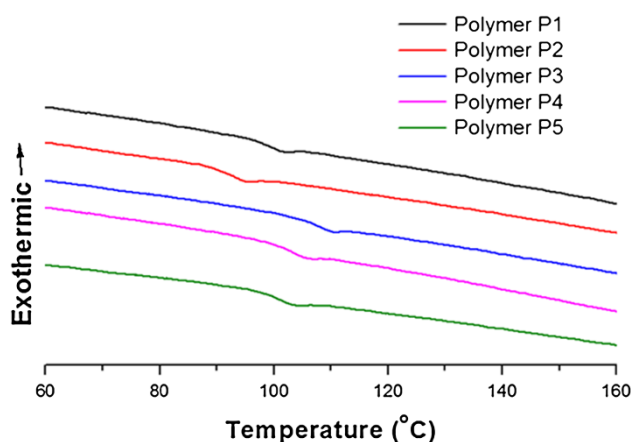
#### (a) Thermal mediated cross-linking

FAVE polymers with enchainned fluoro-olefins show induced thermal cross-linking of internal fluoro-olefins on heating to  $>325$  °C [23]. Being similar in backbone structure, PFCP polymers were also tested for thermal cross-linking. The heating of PFCP aryl ether polymer with biphenyl enchainments to temperature  $>240$  °C gives cross-linked product. Possible cross-linking mechanisms

**Fig. 3** TGA thermograms for polymers **P1–P5**

might involve [2 + 2] cyclodimerization between two PFCP-olefin moieties, [2 + 2] cyclodimerization between PFCP-olefin and the benzene ring, or [4 + 2] cycloaddition reaction between PFCP-olefin (dienophile) and the biphenyl (diene). As experimental results show, the successful thermal cross-linking was obtained only with PFCP aryl ether polymer with biphenyl enchainment, whereas with PFCP polymers with bisphenol A and Bisphenol-6F enchainments do not show any gel formation (Fig. 5). This observation suggests the cross-linking might follow [4 + 2] cycloaddition reaction between diene of biphenyl moiety and dienophile of PFCP ring, and thus the presence of biphenyl (diene) moiety is necessary for network formation. Further studies on the cross-linking mechanism,

**Fig. 2**  $^{19}\text{F}$  NMR of polymer **P1**



**Fig. 4** DSC thermograms for polymers **P1–P5**

extent of cross-linking and reaction conditions are warranted.

(b) Free radical cross-linking

Cross-linking efforts using free radical initiators including AIBN and lauroyl peroxide did not work. As the literature suggests, perfluorocyclic-olefins do not homopolymerize under radical conditions [38]. Therefore, electron deficiency factor combined with steric hindrance factor inhibits the cross-linking of these PFCP polymers via free radical mechanism.

(c) Ionic cross-linking

The PFCP polymers keep the cyclic olefin intact. The literature suggests, in suitable conditions, multiple nucleophilic substitutions on PFCP ring are possible [39]. Model reactions also support the multiple substitutions on PFCP rings (Scheme 7). Model compound 1,2-diphenyl

perfluorocyclopentenyl ether (1) shows two clean signals, corresponding to two kinds of fluorine atoms in a symmetric environment, as expected (Fig. 6a). When the sodium phenoxide reacts with (1),  $^{19}\text{F}$  NMR shows vinyl fluorine signal at 158.6 ppm confirming the third substitution (Fig. 6b). This vinyl fluorine signal goes away with further reaction of (2) with the phenoxide ion.

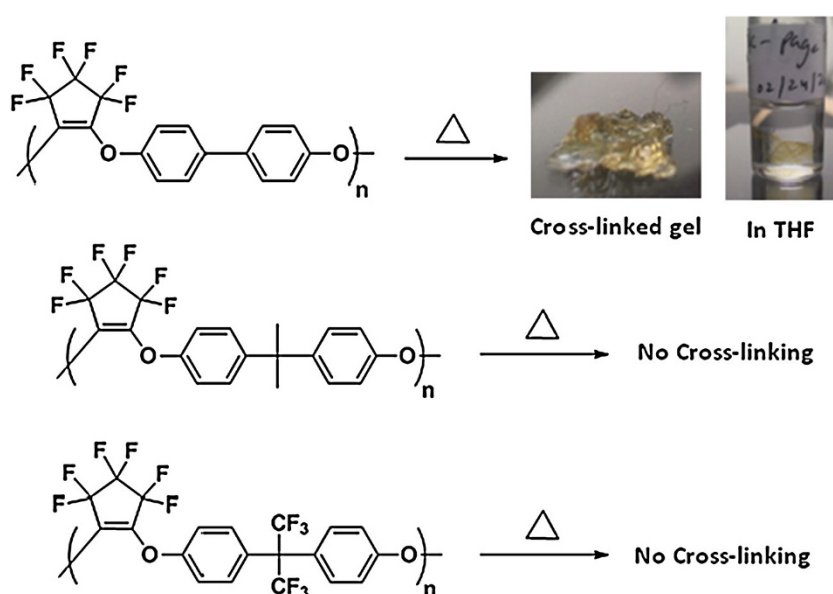
Initial studies show PFCP aryl ether polymers react with dinucleophiles, undergo cross-linking in different reaction conditions and give insoluble products (Scheme 8). Various parameters, including different reaction conditions and different dinucleophiles are under study.

## Experimental details

### Materials and instrumentation

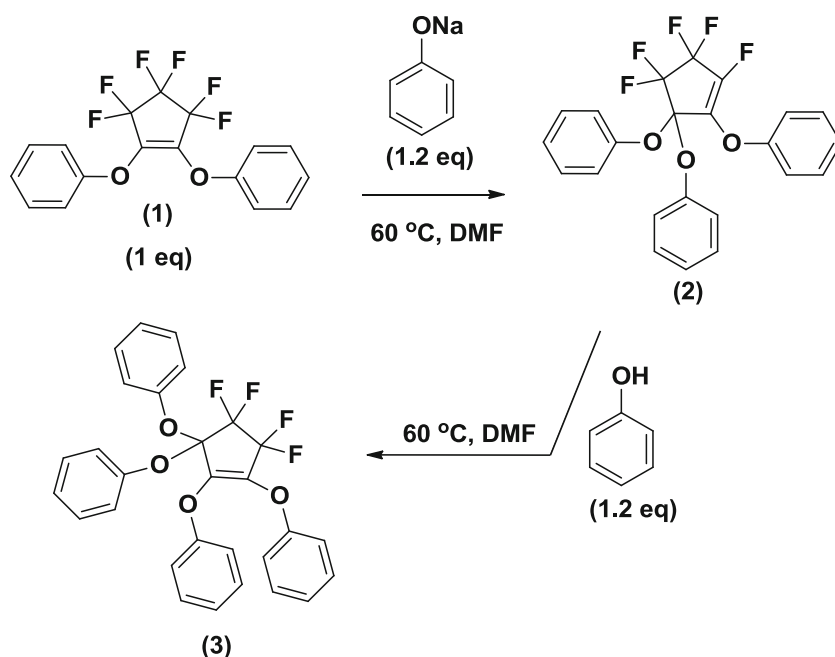
Octafluorocyclopentene and decafluorocyclohexene were purchased from SynQuest Laboratories, while all other chemicals were purchased from Alfa Aesar. Commercially purchased chemicals were used as purchased unless otherwise stated. All synthesized polymers **P1–P5** were characterized by  $^1\text{H}$  and  $^{19}\text{F}$  NMR Spectroscopy, Gel permeation chromatography (GPC), Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) techniques. NMR Spectroscopy was performed on Bruker advanced IIITM 500 MHz spectrometer. Chemical shifts were reported in ppm ( $\delta$ ) with reference to deuterated acetone (2.09 ppm) and trichlorofluoromethane (0 ppm) for  $^1\text{H}$  and  $^{19}\text{F}$  NMR, respectively. GC–MS was obtained on Shimadzu GCMS solution. Analytical thin layer chromatography was performed on EM reagents 0.25 mm silica gel 60-F plates. Molecular weight

**Fig. 5** Thermal cross-linking behavior for PFCA aryl ether polymers





**Scheme 7** Model study for multiple substitutions on PFCA ring



measurements were performed on gel permeation chromatography (Viscotek GPCmax, VE2001) system equipped with a Viscotek TDA 302 Triple Array Detector and two ViscoGEL I-Series (I-MBHMW 3078, Viscotek) columns in series. THF was used as eluent and polystyrene standards were used for calibration. Attenuated total reflectance—Fourier transform infrared (ATR-FTIR) spectroscopy was done on a Thermo-Nicolet Magna 550 FIR spectrophotometer with a high endurance diamond ATR attachment. DSC analysis was performed on a Mettler Toledo DSC 1 system in the nitrogen atmosphere with heating and cooling rate of 10 C/min. The  $T_g$  of polymers were measured from the third heating cycle using Star-E version 10.0 software suite. The thermal stability measurements were performed on a Mettler Toledo TGA/DSC 1 LF instrument, in the nitrogen atmosphere with a heating rate of 10 C/min.

#### Synthesis of monomer (M)

In a flame dried 50 ml single necked round bottom flask, equipped with a magnetic stirrer, 3.84 mmol of bis(4-hydroxyphenyl)phenylamine (**B**), 9.60 mmol of triethylamine and 6 ml of anhydrous DMF were introduced. The solution was purged with nitrogen for 10 min. The solution was heated at 65 °C for 2 h. Let the reaction mixture cooled down to room temperature. This reaction mixture was added to a 6 ml DMF solution containing 9.60 mmol of octafluorocyclopentene, in a 100 ml single necked flask equipped with stirrer, dropwise with a syringe. The solution was stirred at room temperature for next 12 h. Further, the reaction was heated at 65 °C for the next 2 h to ensure the completion of the reaction. The solution was then cooled down, and the pure

product was isolated by column chromatography with pure hexane, as eluent, to give white product (yield = 71 %).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ,  $\delta$ ): 7.18–7.08 (m, 2H), 6.94–6.86 (m, 4H), 6.74–6.65 (m, 7H), 3.37 (brs, 2H).  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ ,  $\delta$ ): –115.64 (m, 8F), –129.72 (brs, 4F), –150.95 (brs, 2F). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 825, 973, 1003, 1,128, 1,195, 1,291, 1,335, 1,364, 1,487, 1,601, 1,727.

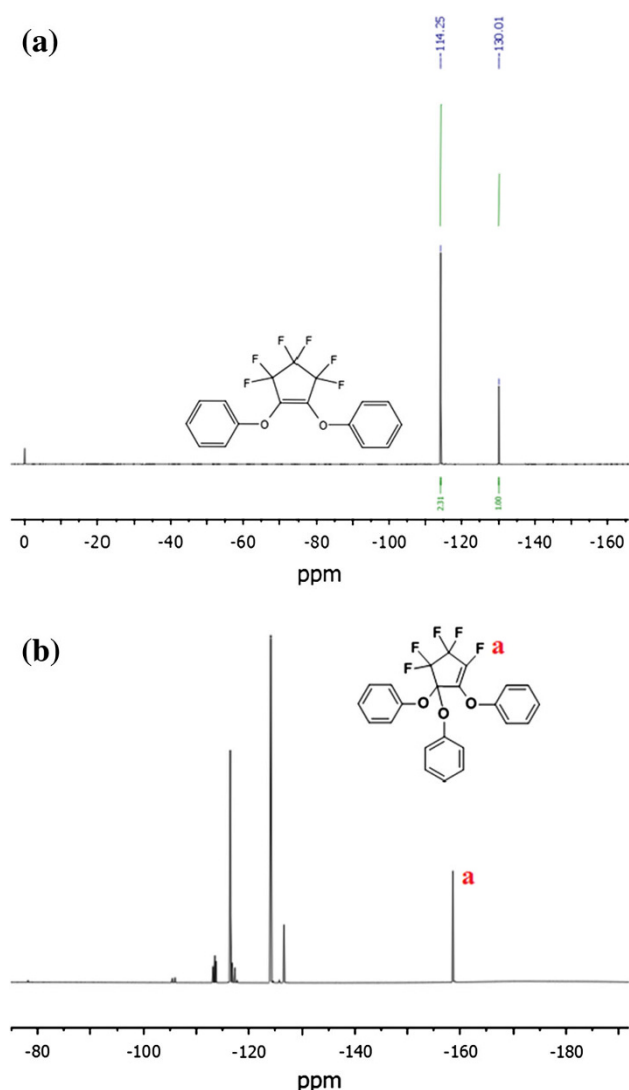
#### Synthesis of polymer P1

To a heat dried 100 ml single necked round bottom flask, equipped with a magnetic stirrer, 0.980 g (1.48 mmol) of monomer (**M**), 0.276 g (1.48 mmol) of biphenol, and 0.679 g (6.67 mmol) of triethylamine was added and then dissolved in 1 ml of anhydrous DMF. The solution was degassed with nitrogen for 10 min and the flask was heated slowly to 80 °C for 36 h under stirring. The dissolved polymer was then precipitated in 100 ml of methanol and washed again with the same, giving a white powder after drying (yield = 81 %).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ,  $\delta$ ): 6.61–7.70 (m).  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ ,  $\delta$ ): –113.59 (4F), –114.38 (4F), –129.74 (4F). FTIR ( $\delta$   $\nu$ ,  $\text{cm}^{-1}$ ): 823 (aromatic C–H), 1,080–1,285 (C–F and C–O–C), 1,497 and 1,599 (aromatic C=C), and 1,686 (C=C).

#### Synthesis of polymer P2

Polymer P2 was synthesized using the same method as P1, giving a white powder after drying (yield = 85 %).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ,  $\delta$ ): 1.58 (brs, 6H), 6.63–7.39 (m).  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ ,  $\delta$ ): –114.20 (8F), –129.73 (4F). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 831 (aromatic C–H),





**Fig. 6** **a**  $^{19}\text{F}$  NMR for 1,2-diphenyl perfluoropentenyl ether (1); and **b**  $^{19}\text{F}$  NMR of the crude reaction mixture showing third substitution

1,080–1,285 (C–F and C–O–C), 1,497 and 1,595 (aromatic C=C), and 1,686 (C=C).

#### Synthesis of polymer P3

Polymer P3 was synthesized using the same method as P1, giving a white powder after drying (yield = 80 %).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ,  $\delta$ ): 6.70–7.40 (m).  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ ,  $\delta$ ): –63.35 (6F), –113.88 (4F), –114.74 (4F), –129.69 (4F). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 827 (aromatic C–H), 1,080–1,285 (C–F and C–O–C), 1,498 and 1,603 (aromatic C=C), and 1,688 (C=C).

#### Synthesis of polymer P4

A mixture of phosphorous oxychloride (0.3 ml) and 0.45 gram of polymer **P1** were dissolved in 15 ml anhydrous

DMF under the nitrogen atmosphere. The reaction mixture was heated for next 5 h at 90 °C. The reaction mixture was cooled down and poured in  $\text{H}_2\text{O}$  to complete the reaction and precipitate the polymer. Polymer was filtered after 1 h of stirring and dried under vacuum (yield = 75 %).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ,  $\delta$ ): 6.59–7.59 (m), 9.78 (s).  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ ,  $\delta$ ): –113.61 (4F), –114.40 (4F), –129.76 (4F). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 825 (aromatic C–H), 1,080–1,285 (C–F and C–O–C), 1,498 and 1,596 (aromatic C=C), 1,691 (C=C) and 1,706 (C=O).

#### Synthesis of polymer P5

Polymer **P1** (0.49 gram) and tetracyanoethylene (0.23 gram) were dissolved in 15 ml anhydrous DMF under nitrogen atmosphere. The reaction mixture was stirred for next 12 h. The product was then precipitated in  $\text{H}_2\text{O}$  and washed with methanol. The purple colored polymer was filtered and dried under vacuum (yield = 79 %).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ,  $\delta$ ): 6.52–7.59 (m).  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ ,  $\delta$ ): –113.66 (4F), –114.36 (4F), –129.80 (4F). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 825 (aromatic C–H), 1,080–1,285 (C–F and C–O–C), 1,496 and 1,597 (aromatic C=C), and 1,689 (C=C).

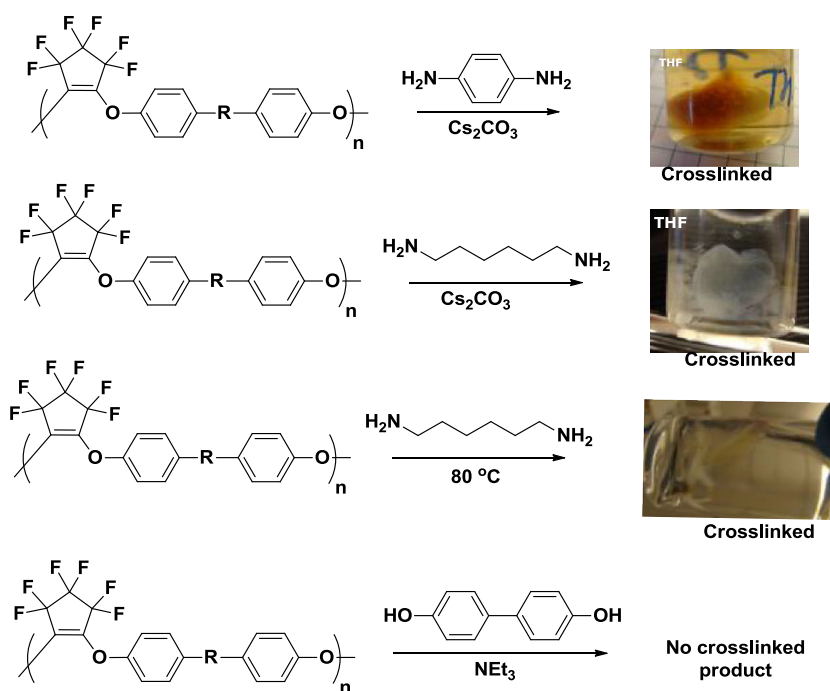
#### Conclusion

We have developed a step-growth polymerization of bisphenols with PFCA towards synthesis of a new class of PFCA aryl ether polymers from commercial feedstock. PFCA aryl ether polymers can be easily modified and functionalized using bisphenols with different spacer functional groups. PFCA aryl ether polymers exhibited very interesting thermal properties with variable  $T_g$  depending upon the chosen bisphenol. These polymers were obtained in good yields and show high thermal stabilities under nitrogen atmosphere. Successful conversion of the newly synthesized TAA enchaind PFCA aryl ether polymers via formylation and EAS demonstrated the synthetic versatility of TAA moiety and provides an excellent option for application specific post polymerization reactions.

PFCA aryl ether polymers with biphenyl units also demonstrate cross-linking behavior upon thermal activation. Exact mechanistic details for this thermal cross-linking are still unknown and further investigations are warranted. Also, PFCA aryl ether polymers undergo ionic cross-linking upon treatment with strong dinucleophiles.

Future studies include the mechanistic studies on the cross-linking behavior of PFCA aryl ether polymers, full chromophorization on TAA units of these successfully

**Scheme 8** PFCP aryl ether polymers undergo cross-linking on treatment with dinucleophiles



synthesized PFCP aryl ether polymers, and their incorporation in electro-optics and photonic devices.

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